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NOVEL NONLINEAR LASER DIAGNOSTIC TECHNIQUES

Gregory W. Faris, Jay B. Jeffries, and D. L. Huestis
Molecular Physics Laboratory

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Air Force Office of Scientific Research
Building 410
Bolling AFB, DC 20332-6448

Attn: Dr. Julian Tishkoff

Approved:

Donald J. Eckstrom, Laboratory Director
Molecular Physics Laboratory

David M. Golden
Vice President
Physical Sciences Division

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G. W. Faris, J. B. Jeffries, and D. L. Huestis

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13. ABSTRACT *(Maximum 200 words)*

This report describes reseach on novel laser-based diagnostic techniques in two areas: (1) extension of laser-based diagnostics to shorter wavelengths, allowing two-photon detection of atomic ions; and (2) investigation of the feasibility of obtaining quantitative concentration and velocity measurements using amplified spontaneous emission (ASE). For the first task, we have developed a high power vuv source based on two-photon-resonant difference frequency mixing of a ArF excimer laser and a frequency-doubled Nd:YAG-pumped dye laser in krypton gas. Up to 6 μJ at 147 nm have been generated, and the characteristics of the mixing process have been studied. On the second task, we have performed the first measurement of the ASE bandwidth, indicating that temperature and velocity measurements may be possible. Measurement of ASE in a variety of flames demonstrate that the ASE signal intensity can be influenced by gas collisions.

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CONTENTS

OBJECTIVES

TASK 1

The research for Task 1 is centered on the extension of laser-based diagnostics to shorter wavelengths. The objectives of this task include the development of new vuv laser sources and techniques, with emphasis on widely tunable radiation with high powers, and the application of this vuv radiation to diagnostics of species not accessible with current visible and near ultraviolet laser sources.

TASK 2

The objective of Task 2 is to investigate the feasibility of obtaining quantitative concentration and velocity measurements of atomic hydrogen and oxygen using the method of laser-excited amplified spontaneous emission (ASE). The approach is as follows:

a. Use pulsed laser two-photon excitation of H atoms, and measure the gain on subsequent ASE using a probe laser.

b. Determine the influence of gain narrowing on Doppler velocity measurements by measurement of the excitation bandwidth with sub-Doppler excitation.

c. Explore the possibility of obtaining velocity or temperature measurements—or both—from the bandwidth of the ASE signal from H and O atoms when the atom is excited with a laser bandwidth wide enough to excite the entire Doppler broadened transition.

d. Make simultaneous laser-induced fluorescence (LIF), resonance enhanced multiphoton ionization (REMPI), four wave mixing, and ASE measurements to understand the influence of the ASE loss process for standard LIF and REMPI measurements.

STATUS OF RESEARCH

TASK 1

Approach and Progress to Date

Advances in laser techniques and technology have been a strong driving force in the development of nonintrusive diagnostic techniques. The production and use of higher laser powers at shorter wavelengths has been particularly fruitful throughout the 1980s and has led to the now well-established techniques of planar laser-induced fluorescence, two-photon-excited fluorescence, and resonantly enhanced multiphoton ionization. More recent advances in nonlinear crystals, such as the materials β-BaB_2O_4 (BBO) and LiB_3O_5 (LBO), allow use of these techniques on species requiring shorter wavelengths.

Below 200 nm, the generation and application of laser radiation become more difficult for two reasons: the lack of suitable nonlinear frequency converting crystals and the increasing absorption of background gases in this region. However, a number of diagnostic problems can only be solved in the vuv. Some species, such as light atomic ions, can only be excited by two photons with vuv radiation (three-photon-resonant excitation is possible in principle, but the process is very weak and the required laser intensities are correspondingly very large). For light atoms and molecules, single-photon vuv excitation offers an alternative to two-photon excitation that has several advantages. Because high intensities are not required, photodissociation and other perturbing processes can be avoided. Quantitative results are simpler to obtain because the process is linear and the transition strengths are often well known. The single-photon sensitivity is higher for single-photon vuv excitation, and planar imaging may be possible. Diagnostic techniques employing vuv will be useful for plasma diagnostics, the study of chemical dynamics and kinetics of processes important in combustion and fluid flow, the calibration of other diagnostic techniques, and the study of shock-heated flows.

A key part of this research is the production of high power vuv radiation suitable for diagnostics measurements. Because of the lack of suitable nonlinear crystals for vuv generation, frequency conversion must be performed in gases. Since gases are centrosymmetric, four-wave mixing is the lowest order frequency conversion process that may be used. To obtain high powers, techniques using resonances are required, such as multi-order anti-Stokes Raman shifting and two-photon-resonant sum and difference frequency mixing.

Under a previous contract, Faris and coworkers (1990) investigated multi-order Raman shifting for the two-photon excitation of atomic and molecular fluorine. Wavelengths as short as 170 nm have been produced. However, the Raman shifting has limitations for vuv generation, including low efficiency for shorter vuv wavelengths, large intensity fluctuations when shifting dye lasers, and limited tuning range when shifting excimer lasers. Raman shifting can be the most appropriate source for certain applications—for example, when the wavelengths required lie within the tuning range of one of the Raman orders for shifting the ArF laser. An example of such a fortuitous overlap is shown in Figure 1, which shows a two-photon spectrum of the $F^1\Pi_g$ (v'=3) state of molecular fluorine excited from the ground state. The ArF laser is tunable through only 1 nm, yet a spectrum of the full band of this vibrational level is possible. This limited tuning of the ArF laser is important for the four-wave-mixing process we currently use for vuv generation.

The two-photon-resonant difference and sum process is shown in Figure 2. Because of the two-photon resonance, this mixing process can provide efficiencies of about 10^{-4}, significantly better than frequency tripling. However, unlike frequency tripling, this process has the disadvantage that two lasers are required. For vuv generation, the difference frequency process is preferable because much of the vuv spectral region may be covered and negative dispersion of the medium is not required. The difference frequency process has been demonstrated using the $5p[5/2,2]\leftarrow 4p^6\ ^1S_0$ (Hilber et al., 1987) and $5p[1/2,0]\leftarrow 4p^6\ ^1S_0$ (Marangos et al., 1990) resonances in krypton with frequency-doubled dye laser radiation as the two-photon pump laser. Because the vuv output power scales as the square of the two-photon pump laser intensity, and minimal tuning of the pump laser is required, a frequency-doubled dye laser may not be the best pump laser. By coincidence, there are two-photon resonances in krypton, H_2, and HD that are within the tuning range of the ArF laser. Because of the very high powers attainable from the ArF laser, this is an attractive pump laser for two-photon resonant difference frequency generation. Use of the $6p[3/2,2] \leftarrow 4p^6\ ^1S_0$ transition for vuv-xuv generation with an ArF laser was proposed by Hilbig et al. (1986) but has not been demonstrated. Two-photon-resonant sum frequency mixing using the E,F(v'=6) $^1\Sigma_g^+ \leftarrow X\ ^1\Sigma_g^+$ (v'=0) Q(1) transition with an ArF laser has been demonstrated for xuv generation (Okada et al., 1990), but two-photon-resonant difference frequency generation of vuv using an ArF laser has not been demonstrated.

For our work on two-photon-resonant difference frequency mixing, we take advantage of previous work on Raman shifting, for which we have performed a number of modifications to a Lambda Physik 150 dual discharge excimer laser to obtain better spatial mode quality (Faris et al., 1990). We use the same laser for two-photon-resonant difference frequency generation. The apparatus is shown in Figure 3. The ArF excimer laser is run as an oscillator-triple pass amplifier. Two mirrors and a pinhole between the oscillator and amplifier are used to filter the beam spatially

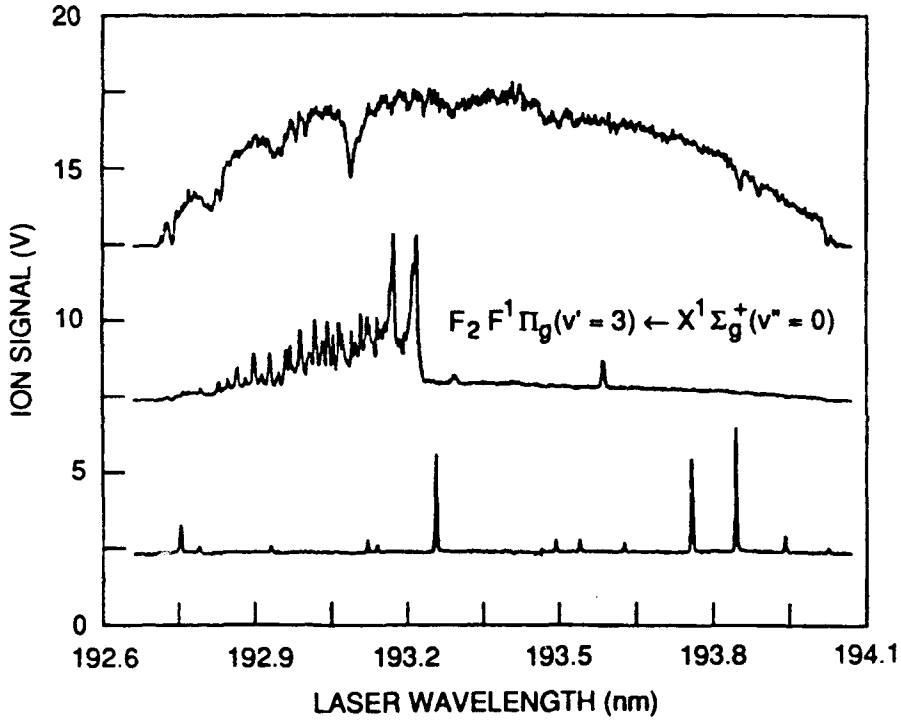

Figure 1. Two-photon spectrum of the $F^1\Pi_g(v'=3) \leftarrow X^1\Sigma_g^+(v'=0)$ transition of F_2.

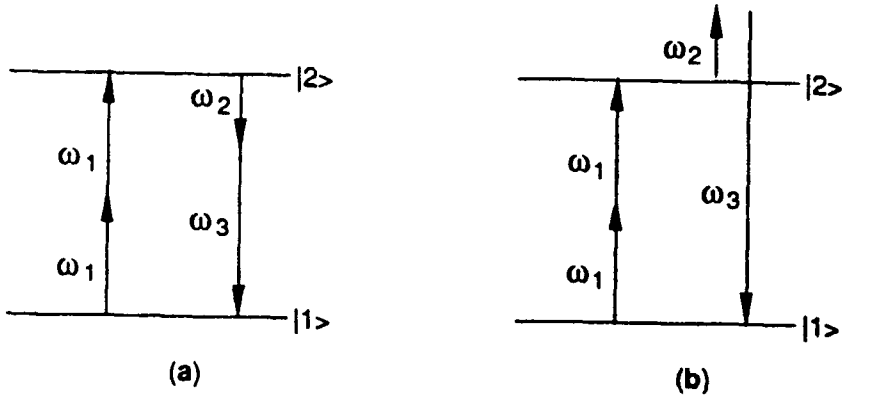

Figure 2. Two-photon-resonant difference- (a) and sum- (b) frequency mixing.

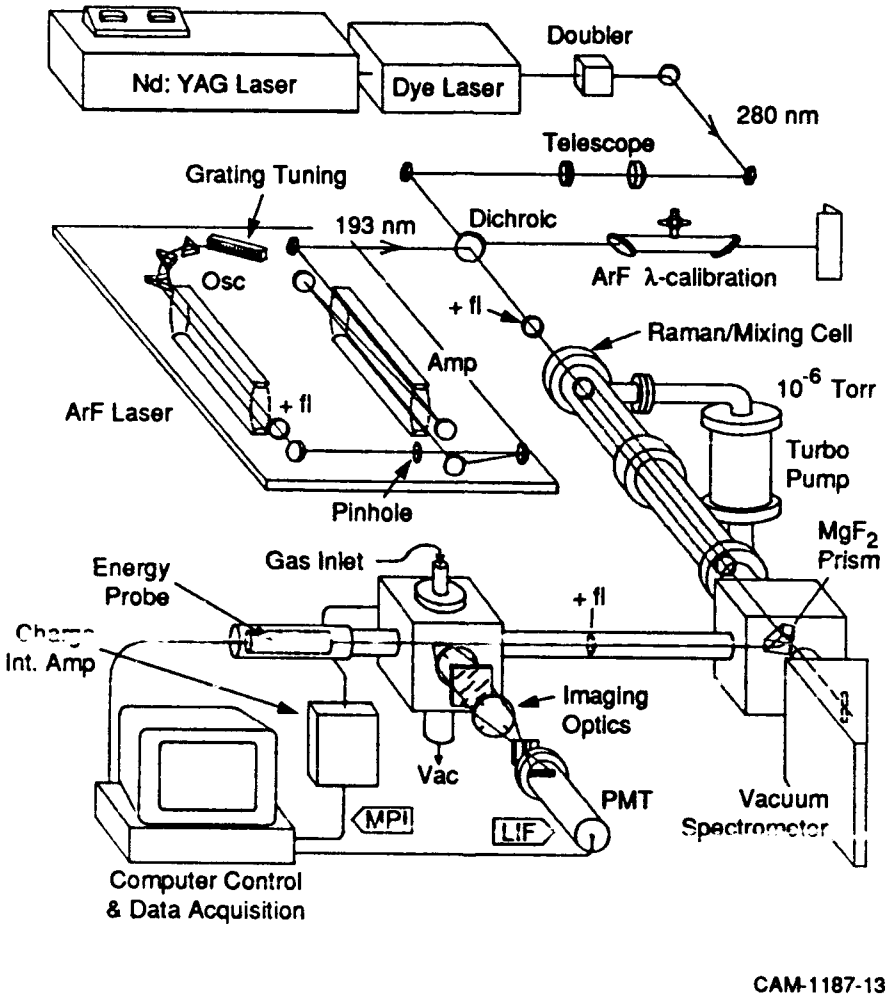

Figure 3. Experimental arrangement for two-photon-resonant difference frequency generation.

and magnify the beam size. The output, up to 60 mJ in a beam five times over the diffraction limit, is combined on a dichroic beamsplitter with the frequency-doubled output of a dye laser (Quanta-Ray PDL) pumped by a Nd:YAG laser (Quanta-Ray DCR II). The timing of the two laser pulses is synchronized to about 2 ns. The two beams are focused together with a 1-m fused silica lens into a gas cell. The beam path of the ArF laser is purged with argon to minimize the effects of oxygen Schumann Runge absorption. From the beam splitter on, the beam path is evacuated. Light passing through the gas cell is collimated with a MgF_2 lens and continues into a vacuum spectrometer or is dispersed with a MgF_2 Pellin Broca prism.

To date, we have only succeeded in performing two-photon resonant difference frequency generation using the $6p[3/2,2] \leftarrow 4p^6\ ^1S_0$ transition in krypton. Our attempts at vuv generation in H_2 using the $E,F(v'=6)\ ^1\Sigma_g^+ \leftarrow X\ ^1\Sigma_g^+\ (v'=0)$ Q(1) transition have been hampered by ASE in the vuv on $B \rightarrow X$ transitions, as has been seen previously (Pummer et al., 1983). The emission we have observed on these bands is shown in Figure 4. Similar ASE behavior is expected in HD, although this has not been investigated.

To date, we have obtained up to 6 μJ at 147 nm by mixing in krypton. This power has been measured with a pyroelectric energy meter after separation of the other wavelengths with the Pellin Broca prism. The power generated in the gas cell is actually much higher (at least 50 μJ), but it is attenuated by absorption by the MgF_2 lens and prism.

The vuv generation in krypton is maximized when the ArF laser is exactly on resonance with the two-photon resonance, as is shown in Figure 5, where the vuv generated at 147 nm and the ionization signal for 2+1 REMPI in a separate krypton cell are shown as a function of detuning of the ArF laser. Examination of the dependence of the vuv intensity on the input laser powers indicates saturation for both lasers. The dependence on the frequency-doubled dye laser power is shown in Figure 6. The power increases proportionally to the first power of the laser power as expected up to about 1 mJ, where saturation begins to occur. The power dependence for the ArF laser, shown in Figure 7, is not fully understood. The power increases as a power of 1.4 over nearly an order of magnitude in laser power before further saturation. The expected power dependence is the square of the ArF laser power, so some saturation is occurring even at low powers. Noninteger laser power dependence has been seen in multiphoton spectroscopy when strong saturation makes the change in laser focal volume the dominant factor that affects the ion signal size, leading to a 3/2 power dependence (Lin et al., 1984). Similar effects may be occurring for this vuv generation, although phase matching considerations are probably more important than volume considerations in determining power dependence.

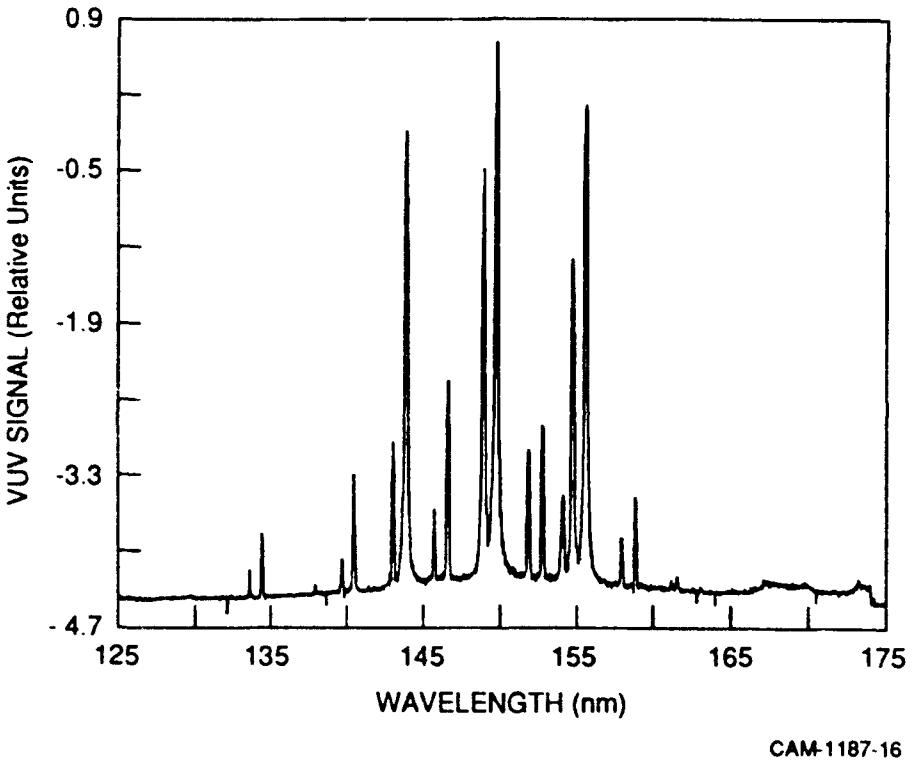

Figure 4. Vacuum ultraviolet amplified spontaneous emission generated on pumping $E,F^1\Sigma_g^+$ (v'=0) ← $X^1\Sigma_g^+$ (v"=0) Q(1) transition in H_2.

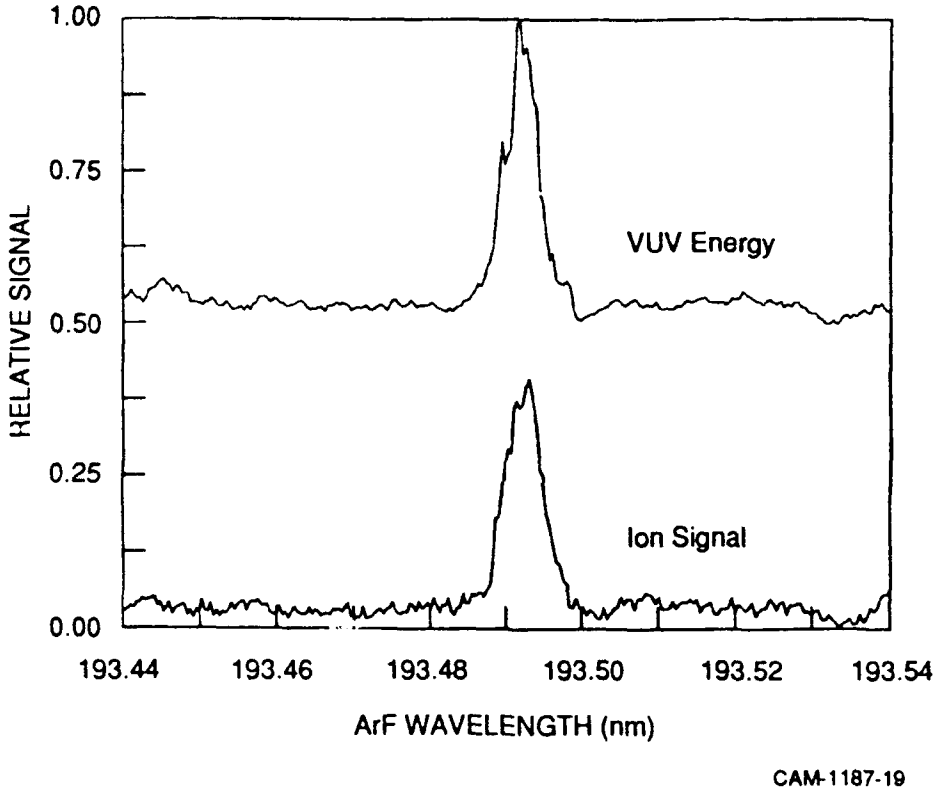

Figure 5. Vacuum ultraviolet energy and 2+1 REMPI in krypton as a function of ArF laser detuning.

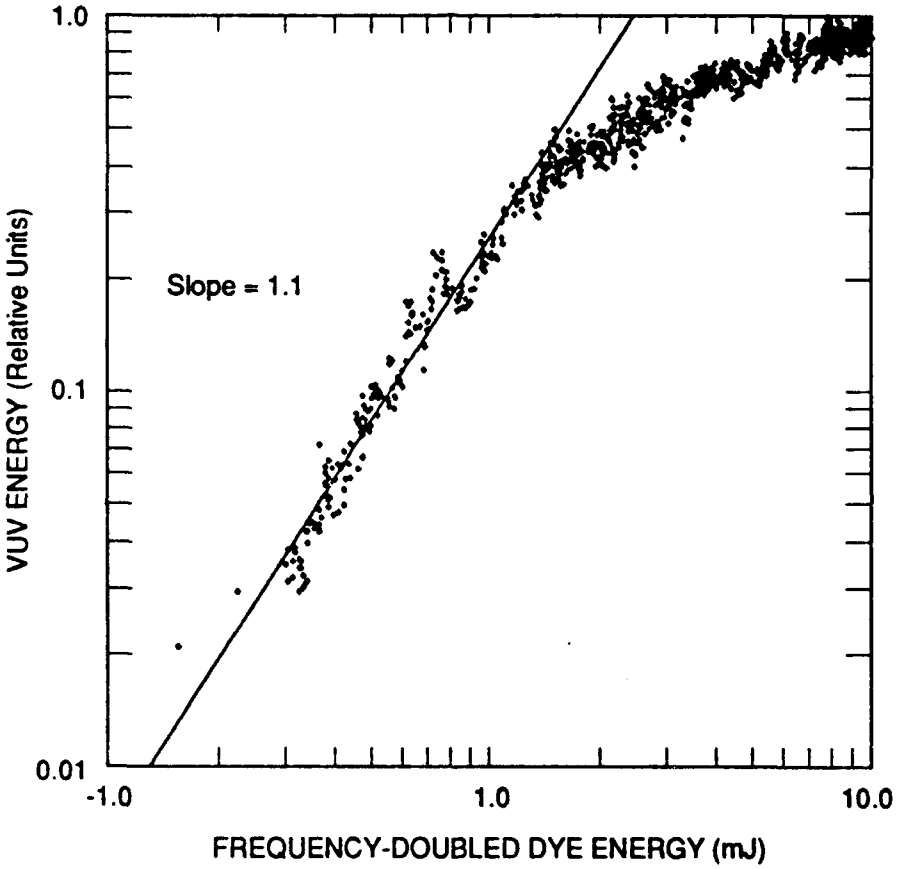

Figure 6. Dependence of vacuum ultraviolet radiation on frequency-doubled dye laser energy.

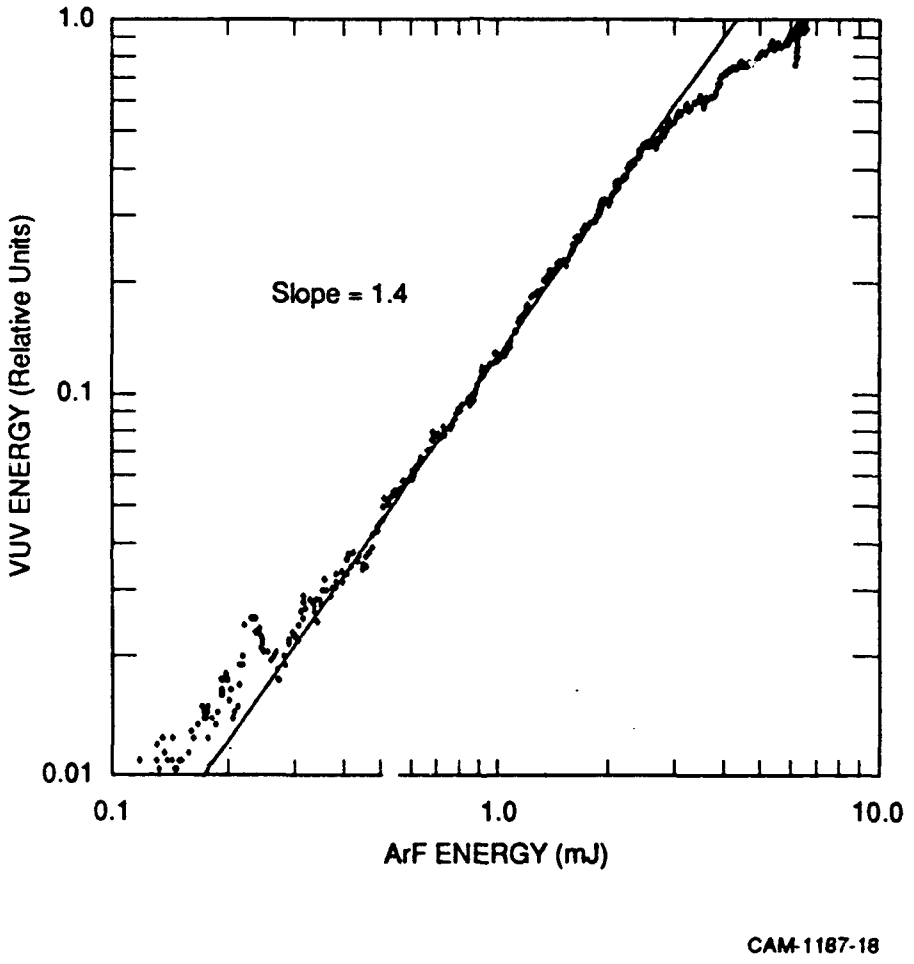

Figure 7. Dependence of vacuum ultraviolet radiation on ArF laser energy.

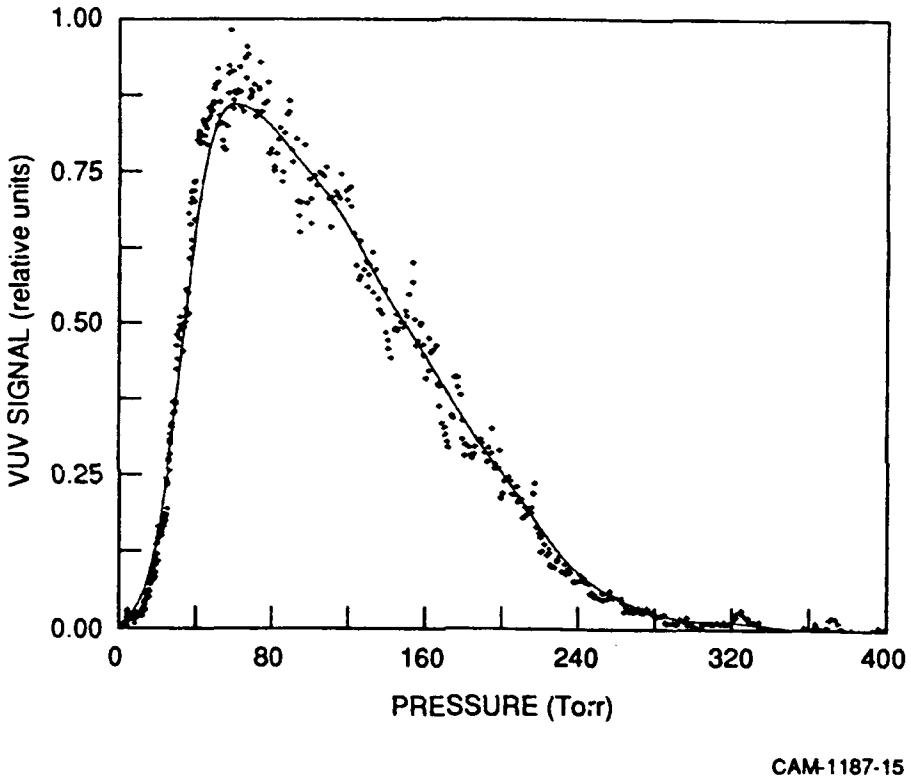

Figure 8. Dependence of vacuum ultraviolet radiation on krypton pressure.

The effects of phase matching are made very clear in the pressure dependence of the vuv power, shown in Figure 8. At low pressures, the vuv power increases as the square of the pressure, as is expected. However, at higher pressures, the power drops off because of the increased importance of phase matching at larger densities. The maximum conversion occurs at a density of about 60 Torr.

The saturation of both input lasers and the loss in conversion efficiency indicate that the vuv generation process is significantly less efficient than is ideally possible. These inefficiencies are ultimately related to phase matching. With better phase matching, we can take better advantage of the quadratic increase in efficiency at higher pressures, and looser focusing can be used, which will reduce the saturation effects that decrease the efficiency. One possible phase matching approach is noncollinear phase matching (Reintjes, 1984). However, because of the large phase mismatch for mixing in the vuv, the crossing angles are large, leading to poor beam overlap. Partial ionization of the gas leads to a negative contribution to the refractive index from the electrons. The electron contribution to the index of refraction becomes more positive at shorter wavelengths, though, and a negatively dispersive correction is required for phase matching. In the region near optical resonances in the vuv, certain gases exhibit negative dispersion, so a mixture of gases can provide phase matching (Harris and Miles, 1971). This procedure may make higher powers possible in limited regions of the vuv.

Conclusions

The first phase of Task 1, the construction of a high power vuv source has been completed, yielding adequate powers for multiphoton excitation in the vuv. Powers up to 6 μJ have been obtained at 147 nm. Krypton appears to be the best candidate for the vuv generation, because ASE occurs in H_2 and HD. The limitations on continuous tuning in the regions of single-photon resonances in the vuv may make consideration of mixing in H_2 or HD necessary. While further improvement of the vuv source is still possible through better phase matching, the current system allows us to proceed to the demonstration of multiphoton vuv excitation.

TASK 2

The first year of this task yielded three significant new results concerning the use of laser-excited ASE as a diagnostic measurement tool for supersonic/hypersonic fluid flow. First, we made the first-ever measurement of laser-excited ASE bandwidth by using a low-pressure flame to provide a source of hydrogen atoms. These preliminary measurements show that single-laser-pulse, single-laser-wavelength gas temperature measurements in reacting flows may be possible

using ASE. Second, these measurements show that the ASE signal is sufficiently collimated and intense for velocity measurements based on the Doppler shifted frequency of the Balmer α transition. Third, other measurements of ASE in a variety of flames show that the ASE signal intensity can be influenced by gas collisions, which will complicate quantitative measurements made using ASE intensity.

Significant progress has been made on all four subtasks in the statement of work.

a. We have developed a "frequency tripling" scheme to produce 205-nm light from a YAG pumped dye laser operating at 615 nm and used this light to observe H atom ASE in the low-pressure flames. We determined that gas collisions significantly influence the spontaneous ASE signal intensity, which will complicate ASE intensity measurements to determine atom concentrations. To avoid these complications, we proposed to study direct ASE gain measurements with a probe laser. We now know enough about the spontaneous ASE signal to properly design such experiments.

b. We have not yet begun experiments with sub-Doppler laser excitation. However, we have determined how to measure the ASE bandwidth and demonstrated the measurements with laser excitation that excites the entire Doppler broadened sample of atoms. We have begun the process of purchasing the laser needed for the sub-Doppler excitation.

c. We have measured the ASE bandwidth and determined that gas velocity measurements using ASE wavelength measurements are feasible. We discovered that by reducing the gain length and laser pulse energy, we could measure the ASE bandwidth without significant gain narrowing. This achievement presents the possibility of determining the gas temperature directly from the ASE bandwidth and avoiding the complications of collisions on ASE intensity.

d. We have made simultaneous LIF and ASE measurements of H atoms in a variety of low-pressure flames. We discovered that at our conditions there is no contribution to the signal from four-wave mixing.

We have studied ASE of atomic hydrogen excited by two photons near 205 nm from the ground 1S to the 3S and 3D states. These states have allowed Balmer α transitions near 656 nm to the 2P state; the direct single-photon transition back to the ground state is not allowed. When the two-photon excitation rate is fast enough, a population inversion between the 3(S & D) and the 2P is produced; the resulting amplification of the spontaneous emission produces the ASE signal. Since atoms are excited only along the laser beam, gain over a significant path length only occurs along the laser beam. Thus, the ASE signal has a divergence that is derived from the excitation laser, and the ASE propagates forward and backward along the laser beam.

Low-pressure flames provide an ideal environment to study ASE because they provide stable sources of large concentrations of hydrogen atoms. By choosing flame conditions identical to those used previously in our laboratory to study OH (Kohse et al., 1989), HCO (Jeffries et al.,

1990), and NO (Heard et al.), and using our model calculations of the flame chemistry, we can estimate the partial pressures of all the gas constituents. Thus, the collisional environment is well characterized, and we can study the influence of gas collisions on the ASE signal level. The experimental method and examples of the experimental results are described in detail in Appendix B.

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D. E. Heard, J. B. Jeffries, G. P. Smith, and D. R. Crosley, submitted to Combustion and Flame.

PUBLICATIONS, INVENTIONS, PATENT DISCLOSURES, AND DISCOVERIES

PUBLICATIONS

Task 1

The following publication has been submitted on research supported by this contract:

1. Gregory W. Faris and Mark J. Dyer, "Multiphoton Spectroscopy Using Tunable VUV Radiation from a Raman-Shifted Excimer Laser," to appear in *OSA Proceedings on Short Wavelength Coherent Radiation: Generation and Applications*, Phillip H. Bucksbaum and Natale M. Ceglio, Eds. (Optical Society of America, Washington, DC, 1991).

   (Included as the Appendix.)

Task 2

The following manuscripts, all of which are in preparation, describe work performed in the first year of this contract.

1. D. E. Heard and J. B. Jeffries, "Bandwidth Measurements of Amplified Spontaneous Emission," to be submitted to Optics Letters or Applied Physics B (depending on manuscript length).

2. D. E. Heard, D. R. Crosley, G. P. Smith, and J. B. Jeffries, "Laser-Induced Fluorescence Measurement and Model Calculation of Atomic Hydrogen Concentrations in Low-Pressure Flames," to be submitted to Combustion and Flame.

3. D. E. Heard and J. B. Jeffries, "Amplified Spontaneous Emission as a Quantitative Diagnostic: The Influence of Gas Collisions," to be submitted to Applied Physics B.

Although the data are collected for all three of these manuscripts, significant data analysis and interpretation are still required before these papers will be submitted.

INVENTIONS, PATENT DISCLOSURES, AND DISCOVERIES

Task 1

The following patent disclosure was prepared on an invention developed under this contract:

Multi-gas Calibration of an ArF Laser

Inventors: Gregory W. Faris and Mark J. Dyer

Task 2

The following discoveries were made:

- We discovered that, even with substantial ASE signals, the ASE bandwidth is not significantly gain narrowed if a short gain length is used. This feature makes ASE gas temperature measurements feasible.

- The ASE bandwidth measurement shows that ASE Doppler shift measurements of subsonic/hypersonic gas velocities are possible.

PROFESSIONAL PERSONNEL

The following professional scientists participated in the research supported by this contract:

TASK 1

Gregory W. Faris, Physicist
Co-principal investigator; Task Leader and lead experimentalist for Task 1.

Mark J. Dyer, Physics Associate
Specialist in lasers and nonlinear optics; made many of the major technical accomplishments.

David L. Huestis, Associate Director of the Molecular Physics Laboratory
Co-principal investigator, project supervisor, and technical contributor, especially on theory and spectroscopy.

TASK 2

Jay B. Jeffries, Senior Research Chemical Physicist
Principal Investigator; and Task Leader for Task 2.

Dwayne E. Heard, Postdoctoral Fellow
Laboratory scientist for Task 2.

David R. Crosley, Assistant Director of the Molecular Physics Laboratory
Technical advisor on spectroscopy (angular momentum algebra) and collision dynamics.

Gregory P. Smith, Senior Research Chemical Physicist
Performed model calculations for flame species partial pressures.

PROJECT INTERACTIONS

We have served as informal advisors on aspects of the work supported by this contract in the following technical interactions.

TASK 1

AFOSR/ONR Contractors Meeting on Propulsion, June 11-15, 1990, Atlanta, GA.

1. Conversations with Dr. Bish Ganguli of Wright Research and Development Center on wide-ranging development of diagnostic techniques.

2. Conversations with Dr. H. F. Calcote of Aerochem, Princeton, NJ, on various subjects, including soot formation.

3. Conversations with Dr. Arthur Fontijn of Rensselaer Polytechnic Institute, Troy, NY, on Raman shifting an ArF excimer laser for detection of BF. (These discussions were followed by telephone conversations and written correspondence on the same subject from June through August 1990.)

Professor Karl Welge of the University of Bielefeld, Germany; visit to SRI International in August 1990 to discuss vuv generation from ArF lasers.

Dr. R. N. Compton of Oak Ridge National Laboratory; telephone conversation in September 1990 to discuss detection of F_2, especially by laser production of H_2^+.

Dr. Stefan Kroll of Lund Institute of Technology, Lund, Sweden; written correspondence in October 1990 on Raman shifting an ArF laser for excitation of doubly ionized sulfur.

Dr. Michael Smith of Arnold Air Force Base, TN; telephone conversations on October 4, 1990, and March 5, 1991, on polarization optimization for excimer lasers, frequency drift of narrowband ArF lasers.

Dr. Robert J. Gordon of the Department of Chemistry (M/C 111), University of Illinois at Chicago; written correspondence in November and December 1990 on two-photon detection of F and F_2.

The conference Short Wavelength Coherent Radiation: Generation and Application, April 8-10, 1991, Monterey, CA.

1. Conversations with Dr. Ken Baldwin of Australian National University, Canberra, Australia, on liquid nitrogen colled Raman cells, Raman shifting of excimer lasers, two-photon-resonant four-wave difference frequency mixing.

2. Conversations with Dr. P. B. Corkum of the National Research Council of Canada on two-photon-resonant four-wave difference frequency mixing.

Bernd Nikolaus, Lamda Physik; conversation at SRI International in April 1991 on second anti-Stokes Raman shifting of ArF lasers for clients at Aerodyne interested in imaging at 160-170 nm.

Drs. Richard Miles and Walter Lempert of Princeton University, Princeton, NJ; conversations on Raman shifting, at the Quantum Electronics and Laser Science Conference, Baltimore, MD, May 12-17, 1991.

TASK 2

Dr. Jeffries, principal investigator for this task, was involved during the past year in numerous scientific discussions concerning the ASE work supported by this contract. These interactions include

AFOSR Contractor's Meeting, June 1990

1. Presentation of new ideas for laser-excited amplified spontaneous emission diagnostics during the workshop "Turbulent Reacting Flow," chaired by Dr. Werner Dahm.

2. Numerous conversations with other Air Force contractors.

Workshop on Diagnostics for Hermes Testing Facilities, July 1990, Le Fauga, France.

1. Invited presentation discussing the use of ASE as a velocity measurement.

2. Because the workshop was hosted by Dr. Jean-Pierre Taran of ONERA in Chatillon, France, and was held at the F4 flow facility at Le Fauga, France, there was an opportunity to inspect a large scale test facility and gain a better understanding of the practical difficulties in making optical diagnostic measurements on hypersonic flows.

3. Other speakers at the workshop included researchers from DLR in Stuttgart and Göttingen, Germany; Stanford University; and Sandia National Laboratory.

Visits with Air Force personnel

1. David Weaver of Phillips Laboratory, Edwards AFB; significant discussions at 1990 Air Force Contractor's Meeting, subsequent telephone conversations, and both the Fall and Spring Meetings of the Western States Section of the Combustion Institute.

2. Allan Garscadden, Aero Propulsion and Power Laboratory, Wright Patterson AFB; thorough discussion of ASE work during his May 1991 visit to SRI International.

3. W. M. Roquemore and Tim Edwards, Aero Propulsion and Power Laboratory, Wright Patterson AFB; discussions at both the 1990 and 1991 Air Force Contractors Meetings.

4. Ingrid Wysong, Dayton Research Contractor, Phillips Laboratory, Edwards AFB; significant discussions on ASE and energy transfer work completed when Dr. Wysong was a postdoctoral fellow in the SRI group.

5. Numerous discussions with other Air Force contractors, including substantive discussions and/or laboratory visits with Hanson and Bowman at Stanford, Winter at UTRC, Branch at Colorado, and Long at Yale.

6. Laboratory visits on the subject of supersonic fluid flow with McKenzie at NASA Ames; Taran, Pealat, and Attal-Tretout at ONERA at Le Fauga and Chatillon, France; and Cattolica, Sandia National Laboratory.

PRESENTATIONS

TASK 1

The following conference papers were presented on research supported by this contract. Each of these presentations generated a number of questions and discussions.

1. David L. Huestis, Gregory W. Faris, and Jay B. Jeffries, "Novel Nonlinear Laser Diagnostic Techniques," Contractors Meeting in Propulsion (AFOSR/ONR), Atlanta, GA, June 11-15, 1990.

2. Gregory W. Faris and Mark J. Dyer, "Multiphoton Spectroscopy Using Tunable VUV Radiation from a Raman-Shifted Excimer Laser," Paper TuA10, Short Wavelength Coherent Radiation: Generation and Application, OSA Topical Meeting, Monterey, CA, April 8-10, 1991.

3. Gregory W. Faris, Mark J. Dyer, David L. Huestis, and William K. Bischel, "Two-Photon Spectroscopy in the Vacuum Ultraviolet Using a Raman-Shifted ArF Excimer Laser," Paper QTuI5, Quantum Electronics and Laser Science Conference, Baltimore, MA, May 12-17, 1991.

TASK 2

The following conference talks were presented on research supported by this contract:

1. J. B. Jeffries, "Amplified Spontaneous Emission Velocity Measurements," Workshop on Diagnostics for Hermes Testing Facilities, Le Fauga, France, July 1990.

2. D. E. Heard and J. B. Jeffries, "Measurements of Atomic Hydrogen in Low-Pressure Flames," Western States Section, Combustion Institute, Boulder, CO, March 1991.

3. D. E. Heard and J. B. Jeffries, "Laser Excited Amplified Spontaneous Emission of Atomic Hydrogen in Low-Pressure Flames," Gordon Conference on the Physics and Chemistry of Laser Diagnostics in Combustion, Plymouth, NH, July 1991.

4. D. E. Heard and J. B. Jeffries, "Amplified Spontaneous Emission Measurements of Atomic Hydrogen in Low-Pressure Flames," VII International Laser Science Conference, Monterey, CA, September 1991.

5. D. E. Heard and J. B. Jeffries, "Laser-excited Amplified Spontaneous Emission of Atomic Hydrogen in Low-Pressure Flames," Annual Meeting of the Optical Society of America, San Jose, CA, November 1991.

Appendix A

MULTIPHOTON SPECTROSCOPY USING TUNABLE VUV RADIATION FOR A RAMAN-SHIFTED EXCIMER LASER

Multiphoton Spectroscopy Using Tunable VUV Radiation from a Raman-Shifted Excimer Laser

Gregory W. Faris and Mark J. Dyer
Molecular Physics Laboratory
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025
Phone: (415) 859-4131
Fax: (415) 859-6196

Abstract

Raman shifting an ArF excimer laser in D_2 and HD, and applications to two-photon spectroscopy in the vuv and near-vuv are described. Preliminary results on generation of vuv by two-photon-resonant difference-frequency mixing of an ArF laser and frequency-doubled dye laser are reported.

Multiphoton spectroscopy has proved to be a valuable technique at visible and uv wavelengths, allowing access to high-lying states and the excitation of transitions not allowed for one photon excitation. Using vuv radiation for multiphoton excitation allows probing even higher states, but high powers are required to obtain reasonable signals. Two-photon excitation with vuv radiation has been performed using tunable excimer laser radiation[1] and by Raman-shifting a frequency-doubled dye laser.[2]

We are using the technique of Raman-shifting a tunable ArF excimer laser for the production of high powers in the vuv. Raman-shifting can provide relatively high efficiency for frequency conversion compared to non-resonant four-wave-mixing techniques. By Raman shifting an ArF laser, which provides high energy radiation tunable around 193.4 nm, anti-Stokes orders in the vuv can be obtained with low order Raman shifts. This allows high powers and lower power fluctuations than when using higher order Raman shifting. Raman shifting an ArF laser in H_2 for production of vuv radiation has been reported previously.[3] We have investigated Raman shifting in D_2 and HD. The use of different isotopes of hydrogen for Raman shifting allows greater spectral coverage, compensating in part for the limited tuning range of the ArF laser.

The apparatus used for our experiments is shown in Figure 1. The laser is a Lambda Physik EMG 150 dual discharge laser. Because the laser mode quality is very important for multi-wave mixing, we have made a number of modifications to the laser. The laser is operated as an oscillator triple-pass amplifier instead of an injection-locked amplifier. The output from the oscillator is passed through a spatial filter, which also magnifies the beam.

The beam is then passed through the amplifier discharge in a vertical zigzag path, saturating the amplifier on the last pass. Optimum energies of over 60 mJ have been obtained through pressure optimization of the oscillator and amplifier discharge timing. We have found that depolarization of the beam can be reduced by careful alignment of the excimer laser's MgF_2 windows. This is performed by passing polarized light at 193 nm through the windows and rotating and tightening them to minimize the depolarization. Polarization of 200:1 has been obtained and the pulse-to-pulse amplitude stability is improved.

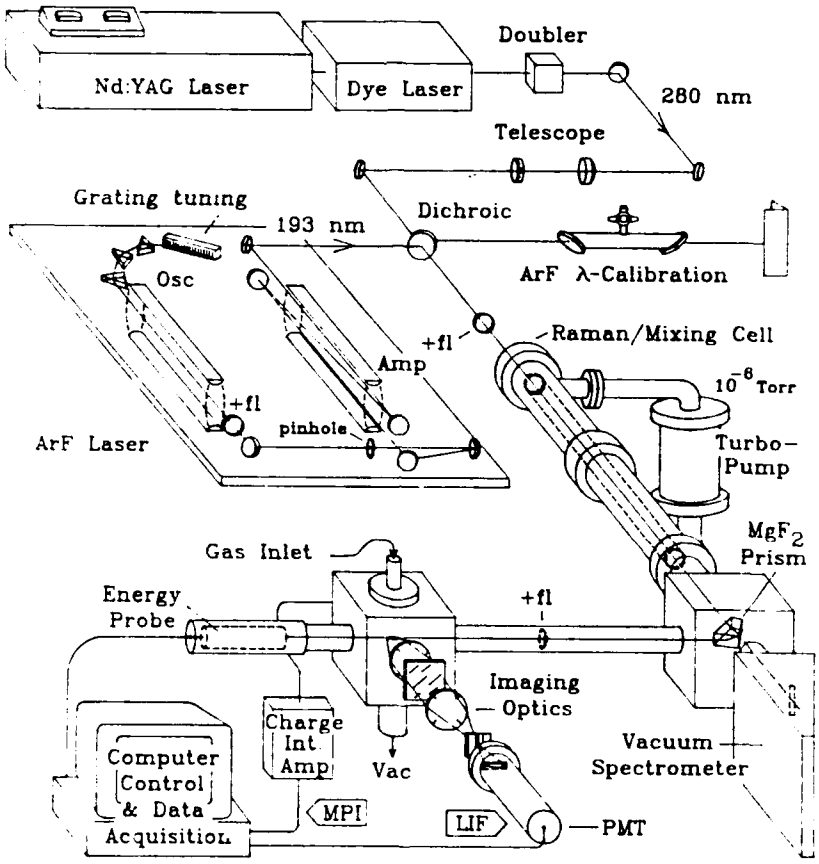

Figure 1. Experimental arrangement for multiphoton excitation using a Raman-shifted using a Raman-shifted excimer laser.

The laser is focused into a cell containing HD or D_2. To minimize absorption from the oxygen Schumann Runge bands, almost the entire beam path up to the cell is either evacuated or purged with argon. Because of the low Raman gain coefficient in HD, the Raman cell is cooled to liquid nitrogen temperature. This cooling increases the gain through redistribution of the HD ground state population, reduction of the Raman linewidth, and reduction of losses as impurities are frozen out. The Raman cell and surrounding liquid nitrogen jacket are contained in a vacuum for insulation and to avoid condensation on the cell windows. The different Raman orders exiting the Raman cell are separated using a MgF_2 prism.

Raman shifting in D_2 at room temperature, we have observed at least eight anti-Stokes orders (to 132 nm) and five Stokes orders. Up to 60% conversion into the first Stokes has

been obtained. In HD at room temperature, 10% conversion into the first Stokes, and low order anti-Stokes were seen. At liquid nitrogen temperature, four anti-Stokes and four Stokes orders have been observed using HD. Competition from rotational Raman scattering and phase matching effects lead to a well defined maximum density for anti-Stokes conversion. By optimizing the second anti-Stokes radiation in HD, we have obtained 1 mJ at 170 nm at a density of 3 amagat.

We have applied the Raman-shifted source to two-photon-resonant excitation of a number of states. Detection is through ions produced by absorption of a third photon. Using the first Stokes radiation in D_2 at about 205 nm, we have excited the $^1\Pi_g$ (v' = 3) state of F_2 from the ground X $^1\Sigma_g^+$ state. This is the central spectrum shown in Figure 2. The band heads correspond to the O and P branches. The top profile in the figure is the power of the first Stokes radiation. The dips in the power are due to Schumann Runge absorption of the fundamental ArF beam in the small length of beam path that is not purged. The bottom trace in the figure is a calibration spectrum for the fundamental ArF beam. It is obtained in a cell containing a mixture of H_2, HD, and krypton, all of which have two-photon resonances within the ArF tuning range. The accuracy of the calibration is limited by the ac Stark effect. We have also observed single lines for two-photon excitation of F atoms and H_2. Using radiation at about 169.67 nm produced as the second anti-Stokes line of ArF in HD we have excited the $^2D^o_{3/2}$ state in atomic fluorine from the $^2P^o_{3/2}$ ground state. A single rotational level of the H,$\bar{H}$ $^1\Sigma_g^+$ has been excited using two photons at about 173.53 nm produced as second anti-Stokes radiation using D_2.

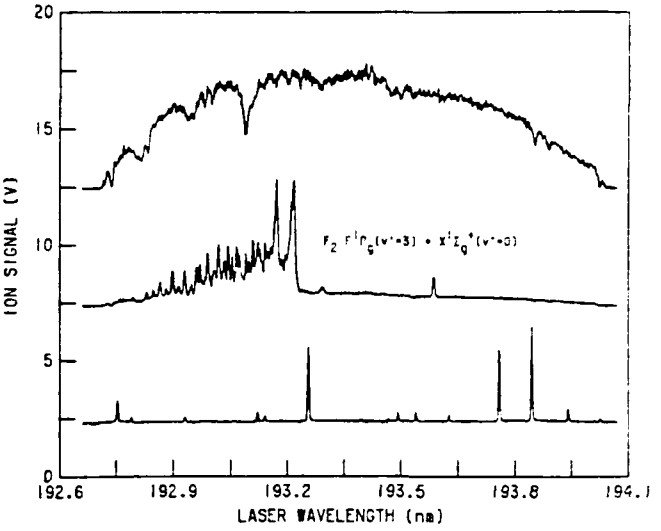

Figure 2. Two-photon resonant spectrum for excitation of the $^1\Pi_g$ (v' = 3) state of F_2. The x axis denotes the fundamental wavelength of the ArF laser.

Through understanding of the Raman process and optimization of the laser beam quality, Raman shifting an ArF excimer laser can provide large energies in the vuv even when shifting in D_2 and HD. The generated vuv power is more than adequate for two-photon spectroscopy.

To produce continuously tunable vuv radiation, we have begun to examine the capabilities of the ArF laser for two-photon-resonant difference frequency generation in krypton. By combining two ArF photons at ω_1 with a photon from a tunable laser at ω_T, vuv photons may be generated through the difference-frequency process

$$\omega_{vuv} = 2\omega_1 - \omega_T.$$

When the two photons at ω_1 lie near a resonance, this process is efficient, as has been shown for the 5p[5/2,2] $\leftarrow$ $4p^6\ ^1S_o$ (Ref 4) and 5p[1/2,0] $\leftarrow$ $4p^6\ ^1S_o$ (Ref 5) resonances. Two-photon resonances for the 6p $\leftarrow$ $4p^6\ ^1S_o$ transitions in krypton lie within the tuning

range of the ArF laser. The high peak powers and good mode quality of the ArF make vuv generation using this technique attractive.

The apparatus for these experiments is also shown in Figure 1. A Nd:YAG-pumped frequency-doubled dye laser is used as the tunable laser. The pulse timing of two lasers is synchronized and they are overlapped using a dichroic mirror. A 1 m lens focuses the two beams into a cell containing krypton. The generated vuv is filtered with a vuv monochomator and detected with a solar blind photomultiplier. Light at 147 nm has been generated. The pressure dependence of the vuv radiation is shown in Figure 3. The optimum pressure is about 60 torr. By varying the input intensities, it is determined that both beams are saturating at the input energies of 6 mJ and 20 mJ for the ArF and frequency-doubled dye lasers, respectively. Experiments to measure the linewidth and energy of the vuv are in progress.

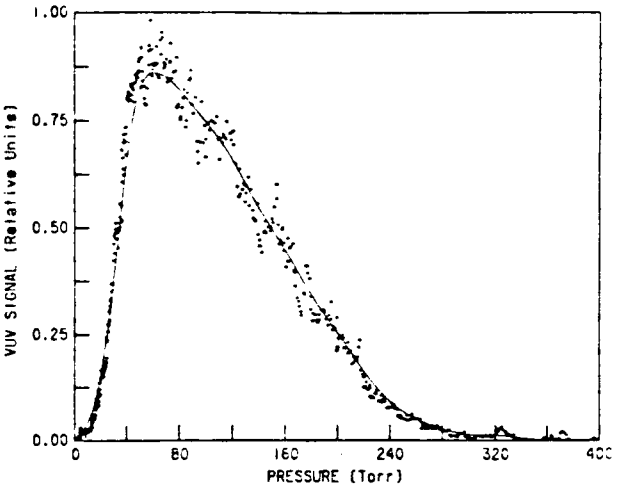

Figure 3. Pressure dependence of vuv radiation.

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Appendix B

MEASUREMENTS OF ATOMIC HYDROGEN IN LOW-PRESSURE FLAMES

MEASUREMENTS OF ATOMIC HYDROGEN IN LOW-PRESSURE FLAMES*

Dwayne E. Heard and Jay B. Jeffries
Molecular Physics Laboratory
SRI International
Menlo Park, California 94025

Measurements of atomic hydrogen have been made in low-pressure methane/air, methane/oxygen, and hydrogen/oxygen flames. These flames have been previously studied[1-5] in our laboratories using laser induced fluorescence to determine spatial distributions of radical species such as OH, CH, CH_2, HCO, and for air flames, NO. The comparison of the measured spatial variation of the concentrations of the radical intermediates to that predicted by a computer model is a sensitive test of the detailed chemical mechanism. In this paper, we present spatial distributions of the hydrogen atom concentrations for these same flames and compare the measurements to predictions of our computer model.

The atomic hydrogen is detected by observing the $n = 3 \rightarrow n = 2$ Balmer α radiation following two-photon laser excitation of the $n = 3$ state.[6] The thermal population of atoms in the $n = 2$ state is nearly zero, and if significant population is excited by the laser to the $n = 3$ levels, a population inversion is created.[7] Indeed, stimulated emission is readily observed[8] in addition to LIF from H atoms in these flames.

Laser light with a wavelength near 205 nm is generated to excite the $n = 3$ state via two photon transitions from the 1S ground state to the 3S and 3D excited states. The 7ns pulses of 615 nm light from a YAG pumped dye laser (Continuum YG-661 YAG and TDL-60 dye laser) are effectively frequency tripled to produce 205 nm light. The dye laser light is first frequency doubled in KD*P. The polarization of the 307.5 nm light is rotated and recombined with the fundamental 615 nm light, and photons from the two beams were sum-frequency-mixed in a beta-barium-borate crystal to produce ~300 μJ pulses of 205 nm light. The 205 nm light was separated from the other colors in a prism and focused with a 10 cm lens into a laboratory flame. Large H atom LIF signals were observed. Fluorescence quenching of the H atoms, even in the lowest pressure, 6 Torr, flames employed, is extremely fast, and the observed lifetime was <20 ns.

The laser light near 307.5 nm used to produce the 205 nm radiation can also be used to

excite the OH radical in the 0-0 band of the A-X transition. Scans of the excitation wavelength monitoring both the H atoms and OH radicals by red and UV fluorescence respectively, showed no exact coincidence between OH and H excitation, as recently reported by Goldsmith.[9] Scanning the near coincident excitation of OH provides a convenient wavelength calibration and provided a simultaneous LIF temperature measurement from analysis of the OH rotational populations.

The flames were supported on a 6 cm diameter, water cooled, McKenna burner in an evacuated housing. Computer controlled motion of the burner allows the H atom LIF signals to be monitored as a function of height above the burner surface. H atom profiles were measured for H_2/O_2, CH_4/O_2, and CH_4/air flames. In the H_2/O_2 flame it was shown that the H atom signal was maximized for a rich stoichiometry. These profiles are currently being measured as a function of laser energy in order to assess possible contributions to the overall LIF signal from H atoms generated by laser photolysis.

If the two-photon excitation rate is large enough, a population inversion between the n = 3 and n = 2 states is possible which can amplify the spontaneous emission. Since the atoms are excited by a small diameter focused laser beam, gain over a significant path length only occurs along the laser beam. Thus, the stimulated emission has a divergence similar to the excitation light and propagates backward and forward along the excitation beam path. We observe the 656 nm stimulated emission (often referred to as Amplified Spontaneous Emission or ASE) from atomic hydrogen by eye on white card, and find it is well collimated as a coherent beam along the laser path. In the forward direction, it is possible to have four wave mixing of two photons from the 205 nm beam, one photon from the $n = 3 \rightarrow n = 2$ transition, and one photon from the $n = 2 \rightarrow n = 1$ transition. However, such four wave mixing can only be phase matched in the forward direction and measurement of a beam of Balmer α light in both the forward and backward direction is used to assess any contribution of four wave mixing to the observed signal.

The H atom LIF and ASE have been simultaneously observed, and the suitability of ASE as a flame diagnostic (the signal is not related to the ground state H atom population in a simple manner) will be investigated by measuring ASE and LIF intensities as a function of height above the burner surface. These comparisons will be compared with an earlier observation of ASE from H atoms in a higher pressure (72 Torr) flame.[8] Due to the brightness and directionality of the coherent ASE beam, single laser shot measurements of the ASE are possible. Measurements to

assess the feasibility of single laser shot concentration and temperature measurements will be discussed.

*Supported by the Air Force Office of Scientific Research.

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